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Effect of electromigration on interfacial reactions between electroless Ni-P and Sn–3.5% Ag solder

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Abstract

Effect of electromigration on interfacial reactions between electroless Ni–P (EL-Ni) and eutectic Sn–3.5% Ag solder has been investigated. Sandwich-type reaction couples, Cu/EL-Ni/Sn–3.5% Ag/EL-Ni/Cu, having two EL-Ni/Sn–3.5% Ag interfaces were prepared with the help of reflow process. During reflow, Ni_3Sn_4 intermetallic formed at the EL-Ni/Sn–3.5% Ag interfaces with a dark thin Ni_3P layer underneath it. The reaction couples were annealed at 160 and 180 °C for various durations with and without the passage of DC current of 1×10^3 A/cm^2 density. It was found that current does not affect the stoichiometry of the intermetallics formed at the EL-Ni/Sn–3.5% Ag interfaces. The same Ni_3Sn_4 intermetallic formed in the samples annealed at both the temperatures with and without current. Formation of Kirkendall voids in the Ni_3P layer showed that Ni diffuses from EL-Ni through the grain boundaries of Ni_3P to form Ni_3Sn_4. It was observed that current retards the Ni_3Sn_4 growth at both the anode and cathode side interfaces at 180 °C, while no significant retardation was observed at 160 °C. This effect of electromigration on the EL-Ni/Sn–3.5% Ag interfacial reactions was due to the presence of Ni_3P layer in between EL-Ni and Ni_3Sn_4.

Keywords: Electromigration; Interfacial reactions; Electroless Ni–P; Solder

1. Introduction

Electromigration, which is a transport phenomenon caused by the passage of electric current through a conductor, results in change of atomic distribution in the conductor. Driving force for this migration is the momentum exchange force, which arises from collision of charge carrier with the conductor atoms [1,2]. In heterogeneous materials system, atomic transport phenomenon also occurs due to the concentration gradient wherein atoms diffuse and form intermetallic compounds (IMC) to obtain the equilibrium situation. The electromigration flux caused by the passage of electric current in the heterogeneous materials system, influences the atomic flux that occurs due to the concentration gradient [4–9]. This electromigration flux is given by the following equation:

$$j_{\mathrm{em}} = \frac{CDZ^{*}e\rho j}{kT} \quad (1)$$

where C is the concentration of moving atoms, D is the diffusivity, k is Boltzmann's constant, T is the absolute temperature, e is the electron charge, Z^* is the effective charge number, ρ is resistivity and j is current density.

Both the mass transport phenomena, electromigration and migration due to the concentration gradient, are very common in interconnects of electronic devices, which carry high current density and have interfaces between different materials such as solder/under bump metallization (UBM) interface. During soldering, initial formation of IMC at the solder/UBM interface ensures a good metallurgical bond. However, growth of these IMC affects the mechanical reliability of the interface [3]. Most of the interfacial studies between solder and UBM are based on annealing effect. However, a few investigations have shown that electromigration influences the interfacial reactions in most of the metallic systems [4–9]. Thus, it is significant to investigate the electromigration effect on the interfacial reactions between solder and UBM.

In recent years, electroless Ni–P (EL-Ni) is considered as a promising UBM due to its many advantages such as excellent solderability, good corrosion resistivity, selective deposition, strong adhesion, ease of processing, and low

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cost process as compared to thin-film vacuum processes [10–12]. The interfacial reactions, between EL-Ni and solder alloys, have been studied by number of researchers [11–16]. However, no literature has been found on the effect of electromigration on the EL-Ni/Sn–3.5% Ag interfacial reactions. The present study involves the investigation of electromigration effect on the phase formation and growth of IMC in the EL-Ni/Sn–3.5% Ag system at different temperatures.

2. Experimental procedure

In order to investigate the electromigration effect upon EL-Ni/Sn–3.5% Ag interfacial reactions, Cu/EL-Ni/Sn–3.5% Ag/EL-Ni/Cu reaction couples having two EL-Ni/Sn–3.5% Ag interfaces were prepared as follows. First, a piece of commercial copper plate of the size 7 × 2.5 mm and 3.0 mm in thickness was ultrasonically cleaned in acetone for 20 min to remove the organic impurities. The plate was then etched with 30 vol.% HNO_3 solution for 2 min to remove inorganic impurities and surface oxide. Surface cleaned Cu plate was coated by EL-Ni in two steps. In the first step, Cu surface was activated using the ruthenium-based commercial pre-initiator. Then, EL-Ni was coated on the activated Cu surface using commercial electroless nickel solution. Thin layer (~ 200 Å) of non-cyanide immersion gold was also deposited on EL-Ni surface to protect the surface from oxidation.

EL-Ni coated Cu plate was cut into two pieces of size 4.5 × 2.5 mm and 2.5 × 2.5 mm. They were then joined with each other using Sn–3.5% Ag solder with the help of reflow process. The reflow was carried out at 245 °C for 60 s. Fig. 1 shows the schematic diagram of setup by which solder joint was formed in between the two EL-Ni coated Cu plates. The joint was formed during the reflow process by placing a number of small pieces of Sn–3.5% Ag solder wires on the small EL-Ni coated Cu plate and pressing them by the big plate. Glass spacers of thickness 450 μm were used to maintain the uniform thickness of Sn–3.5% Ag solder in between the EL-Ni coated Cu plates. The joined plates were cut into 450 μm × 650 μm × 6 mm reaction couples with the help of diamond saw. Fig. 2 shows the schematic diagram of as-prepared EL-Ni/Sn–3.5% Ag reaction couple.

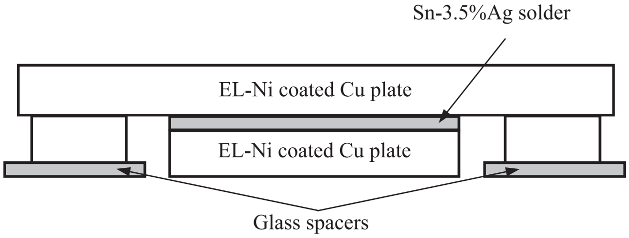

Fig. 1. Schematic illustration of preparation of Cu/EL-Ni/Sn–3.5% Ag/EL-Ni/Cu reaction couples.

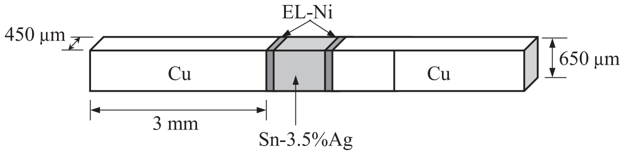

Fig. 2. Schematic diagram of as-prepared EL-Ni/Sn–3.5% Ag reaction couple.

Experimental setup used to pass the electric current through the couple is shown in Fig. 3. As-prepared couple was connected to current source with the help of a specially designed sample holder, which has a ceramic base and two Cu electrodes to hold Cu part of the reaction couple. Upper surface of Cu electrodes was coated with high temperature polymer film to disconnect them electrically from the sample holder body. These Cu electrodes were directly connected to a current source and a thermocouple was kept at the centre of reaction couple using the high temperature thermo-tape to monitor the reaction temperature.

As-prepared reaction couples were annealed at 160 and 180 °C for various durations from 48 to 400 h. DC current of about 1×10^3 A/cm^2 density was also passed through the couple connected to the power source. After annealing with and without the passage of current, the couples were removed from the oven and cooled in air. Scanning electron microscopy (SEM) was used to observe the morphology and to measure the thickness of IMC layer. The thickness was calculated by dividing the IMC's area at the interface with associated interface length. For SEM observation, the couples were cold mounted in epoxy and polished down to 1 μm finish. After polishing, etching was carried out using 4 vol.% hydrochloric acid to reveal the microstructure at the interface. Energy dispersive X-ray (EDX) was performed in the SEM to analyse the chemical composition of EL-Ni and IMC.

3. Results and discussion

3.1. As-prepared reaction couple

Fig. 4a shows the cross-sectional view of as-prepared reaction couple. The measured thickness of the solder layer was around 425 μm. Fig. 4b is the micrograph of EL-Ni/Sn–3.5% Ag interface in as-prepared couple. It shows that IMC with needle and chunky-type morphologies formed at the EL-Ni/Sn–3.5% Ag interface during the reflow. A dark thin layer also formed in EL-Ni layer underneath the IMC. Some voids were observed at the Cu/EL-Ni interface, which formed due to the etching during the surface preparation of the Cu plate. The thickness of EL-Ni and IMC layers were measured to be around 6.5 and 2.5 μm, respectively. EDX analysis showed that the Au layer completely dissolved in the solder during the reflow, as apparent with the absence of Au or Au–Sn IMC at the interface. Fig. 5a–c show the EDX analysis of IMC, EL-Ni layer, and dark thin layer underneath the IMC, respectively. Quantitative EDX analy-

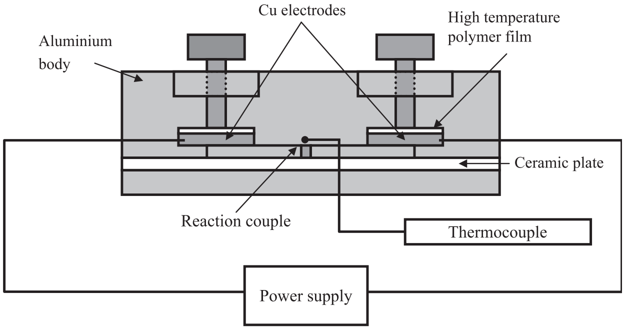

Fig. 3. Schematic diagram of experimental setup used for electromigration study on the EL-Ni/Sn–3.5% Ag reaction couple.

sis showed that IMC has 43.39 at.% Ni and 56.61 at.% Sn, EL-Ni layer has 9.23 at.% P and 90.77 at.% Ni and dark thin layer has 20.85 at.% P and 79.15 at.% Ni. This composition of the IMC and dark thin layer are close to Ni_3Sn_4 and Ni_3P, respectively. Thus, during the reflow needle and chunky-type Ni_3Sn_4 formed at the EL-Ni/Sn–3.5% Ag interface with a P rich Ni_3P layer underneath the Ni_3Sn_4. These results are in agreement with the previous interfacial studies between EL-Ni and Sn–3.5% Ag solder [11–13].

3.2. Growth mechanisms of IMC and Ni_3P layers

Electromigration influences the interfacial reaction in most of the metallic system in terms of phase formation and growth [4–9]. Therefore, the growth mechanisms of IMC and Ni_3P layers in the EL-Ni/Sn–3.5% Ag system have to be understood first. The interfacial reaction between EL-Ni and Sn–3.5% Ag is highly complicated due to the presence of P in EL-Ni. According to the binary phase diagram, the thermodynamic equilibrium phases near the compositions of EL-Ni are Ni_3P and Ni [17], which form in the case of self-crystallization of amorphous EL-Ni at temperatures only above 250 °C [18,19]. However, in soldering reaction-assisted crystallization, Ni_3P forms well below 250 °C, along with the formation of Ni_3Sn_4 as a result of reaction between Ni and Sn [11]. The interfacial reaction between EL-Ni and solder alloy during reflow could be written as

$$\mathrm{Ni}_x\mathrm{P}_y + \frac{4(x-3y)}{3}\mathrm{Sn} \rightarrow y\mathrm{Ni}_3\mathrm{P} + \frac{(x-3y)}{3}\mathrm{Ni}_3\mathrm{Sn}_4 \tag{2}$$

Further growth of Ni_3Sn_4 during annealing requires Ni that comes from the EL-Ni layer thereby increasing the Ni_3P layer thickness. Jang et al. [11] proposed that during Ni_3Sn_4 growth either Ni diffuses out of EL-Ni to Ni_3P/Ni_3Sn_4 interface through the grain boundaries of Ni_3P or Ni_3P decomposes into P and Ni at the Ni_3P/Ni_3Sn_4 interface and the P diffuses interstitially back to grow Ni_3P at the Ni_3P/EL-Ni interface. However, they supported the later mechanism as grain boundary diffusion of Ni must be accompanied by back diffusion of vacancies and they did not find any Kirkendall voids in the Ni_3P layer.

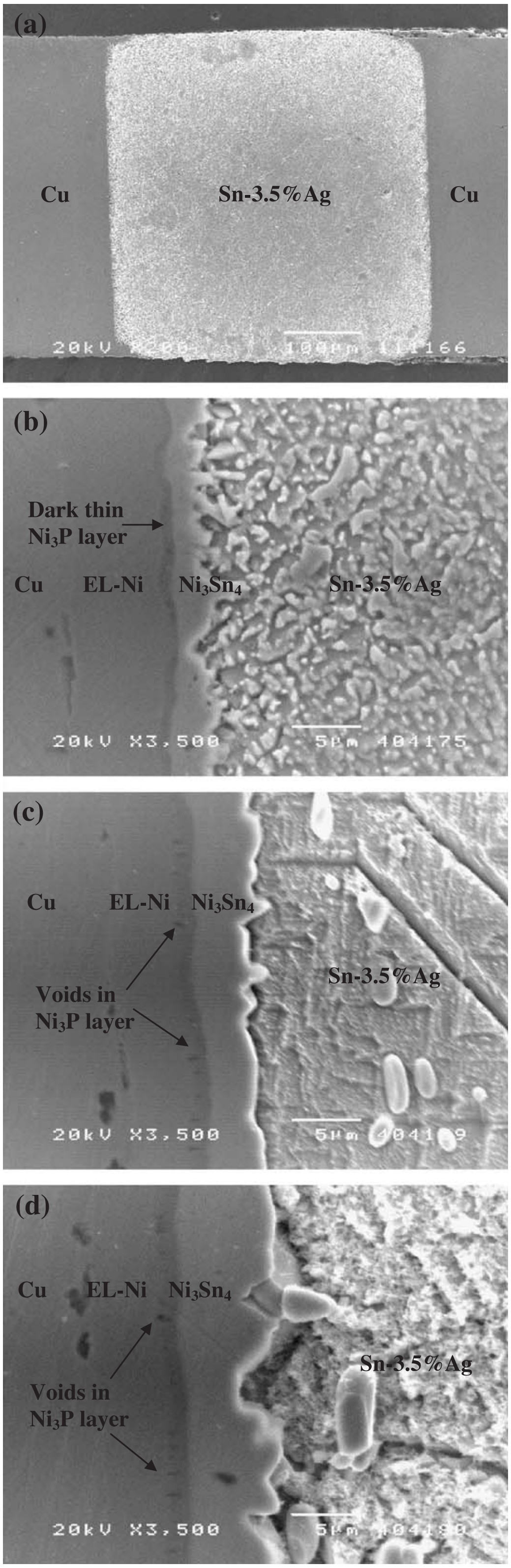

Fig. 4. SEM image of (a) as-prepared couple (b) EL-Ni/Sn–3.5% Ag interface in as-prepared couple (c) EL-Ni/Sn–3.5% Ag interface in the couple annealed at 160 °C for 400 h without current (d) EL-Ni/Sn–3.5% Ag interface in the couple annealed at 180 °C for 400 h without current.

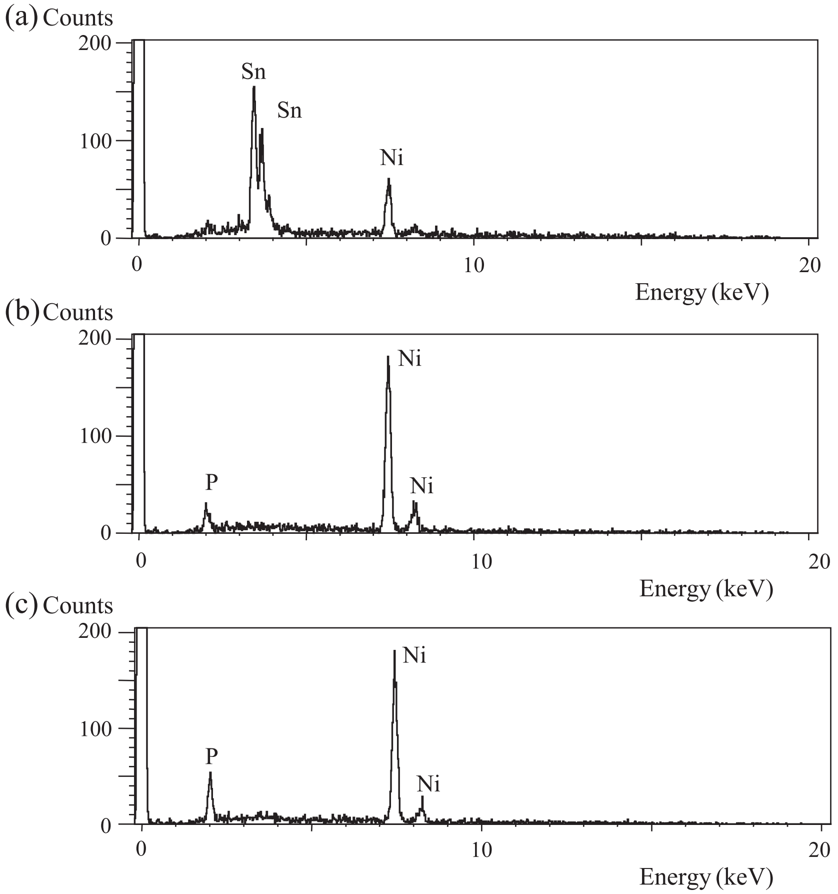

Fig. 5. EDX analysis of different layers formed at the EL-Ni/Sn–3.5% Ag interface of as-prepared couple (a) IMC layer, (b) EL-Ni layer and (c) dark thin EL-Ni layer underneath the IMC.

In this investigation, it was observed that Ni_3P layer has small Kirkendall voids, whose size and number increase with the duration of annealing. Fig. 4c and d, respectively, are the micrographs of EL-Ni/Sn–3.5% Ag interface in the couples annealed for 400 h at 160 and 180 °C without current, showing the formation of large number of voids in the Ni_3P layer. Thus, during solid-state annealing Ni diffuses from EL-Ni to Ni_3P/Ni_3Sn_4 interface through the grain boundaries of Ni_3P layer. This Ni diffusion from EL-Ni layer, results in a counter diffusion of vacancies, which accumulate and form voids in the Ni_3P layer. The depletion of Ni from EL-Ni/Ni_3P interface assists the EL-Ni to crystallize into Ni_3P and increases the Ni_3P layer thickness. The reason behind the invisibility of the voids in the Ni_3P layer in the work of Jang et al. [11] could be the insufficient accumulation time for the vacancies during the brief annealing duration of up to 40 min.

3.3. Effect of electromigration on the interfacial reactions

It was observed that electromigration does not affect the phase formation in EL-Ni/Sn–3.5% Ag system. Ni_3Sn_4 was the only phase formed in all the reaction couples annealed at 160 and 180 °C for various durations, with and without the passage of current. Figs. 6 and 7 are the plots showing the variation in thickness of Ni_3Sn_4 with time in the reaction couples annealed at 160 and 180 °C, respectively, with and without current. In the couple with current, thickness was

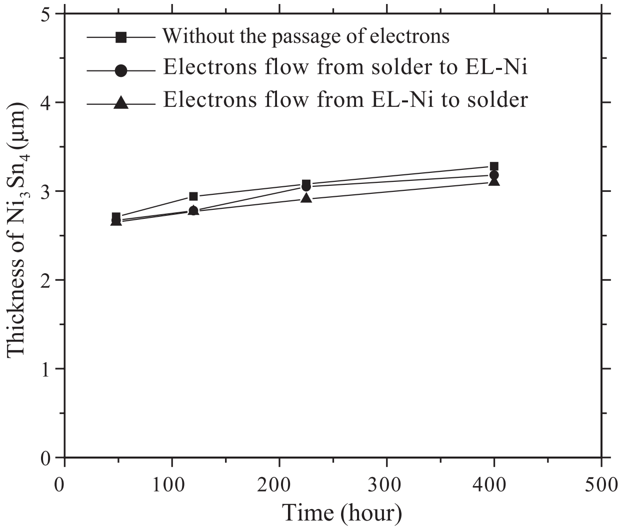

Fig. 6. The thickness of Ni_3Sn_4 as a function of time in the sample annealed at 160 °C, with and without the passage of current 1×10^3 A/cm^2.

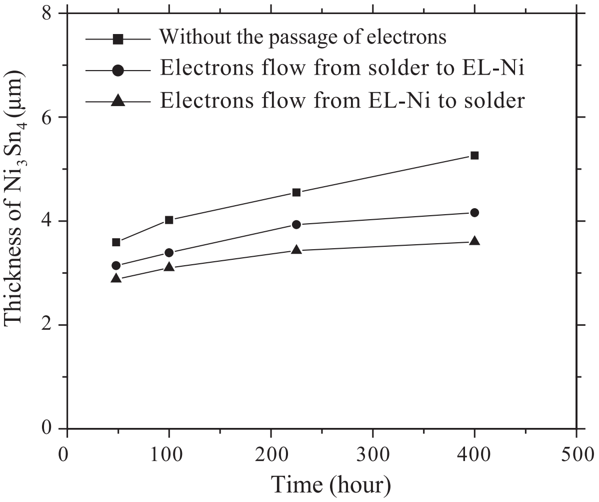

Fig. 7. The thickness of Ni_3Sn_4 as a function of time in the sample annealed at 180 °C, with and without the passage of current 1×10^3 A/cm^2.

measured at both the anode side interface, where electrons flow from Sn–3.5% Ag solder to EL-Ni, and cathode side interface, where they flow from EL-Ni to solder. In the couple without current, Ni_3Sn_4 thicknesses at both the interfaces were nearly the same, therefore only one value was reported for each measurement. Electromigration influenced the growth of Ni_3Sn_4 at both the interfaces by retarding it and this effect was visible at 180 °C (Fig. 7) but negligible at 160 °C (Fig. 6). The absence of electromigration effect at 160 °C is due to the fact that the Ni_3Sn_4 growth was low at 160 °C (at which thickness varied from 2.6 to 3.3 μm) as compared to 180 °C (at which thickness varied from 2.9 to 5.3 μm). The lower growth at l60 °C is understood to be due to the lower diffusivity at 160 °C than at 180 °C.

The growth of IMC in reaction couple depends upon the direction of mass fluxes at the reaction-interface. If fluxes flowing toward the reaction-interface are larger than the fluxes flowing outward, the IMC grow, whereas in the opposite case, they shrink. As mentioned previously, electromigration influences the atomic fluxes in heterogeneous materials system. In most of the systems, it enhances the atomic flux of species when electrons flow in the direction of species diffusion driven by the concentration gradient, whereas retards when electrons flow in the opposite direction. This electromigration effect was investigated in Ni/Sn and Ni/Sn–3.5% Ag systems [4,6,9]. It was observed that electromigration accelerates the Ni_3Sn_4 growth when electrons flow in the direction of Sn diffusion and when they flow in the opposite direction it retards the Ni_3Sn_4 growth [4]. It was found that electromigration influences the Sn flux through Ni_3Sn_4, whereas it does not have significant affect on the Ni flux through Ni_3Sn_4. Similar explanation was reported for the electromigration effect in the Ni/Sn–3.5% Ag system [6].

In EL-Ni/Sn–3.5% Ag system, as mentioned in the previous section for Ni_3Sn_4 growth Ni comes from EL-Ni layer to Ni_3P/Ni_3Sn_4 interface through Ni_3P layer, which plays an important role in the electromigration effect upon the EL-Ni/Sn–3.5% Ag interfacial reactions. Fig. 8 illustrates the electromigration effect on Ni_3Sn_4 growth in the EL-Ni/Sn–3.5% Ag system. When current passes through the Cu/EL-Ni/Sn–3.5% Ag/EL-Ni/Cu reaction couple, at the anode side interface, electromigration retards the Ni flux through the Ni_3P towards the Ni_3P/Ni_3Sn_4 interface, whereas at the cathode side interface, it retards the Sn flux through the Ni_3Sn_4 towards the Ni_3Sn_4/Ni_3P interface. As a result the Ni_3Sn_4 growth is less at both the interfaces, compared with the couple without the passage of current. Significant effect of electromigration on the Ni flux in the EL-Ni/Sn–3.5% Ag system, unlike in the Ni/Sn and Ni/Sn–3.5% Ag systems, is expected due to the high resistivity of EL-Ni, which is one order of magnitude higher than that of pure Ni [20, 21].

3.4. Conclusion

In EL-Ni/Sn–3.5% Ag system, only one Ni_3Sn_4 IMC formed at the interface during annealing at 160 and 180 °C with and without the passage of current of 1×10^3 A/cm^2 density. The electric current does not show significant affect on Ni_3Sn_4 growth at 160 °C since the diffusion activity at this temperature is relatively low. However, at 180 °C it retards the Ni_3Sn_4 growth at both the anode and cathode side interfaces. This effect of electromigration on the EL-Ni/

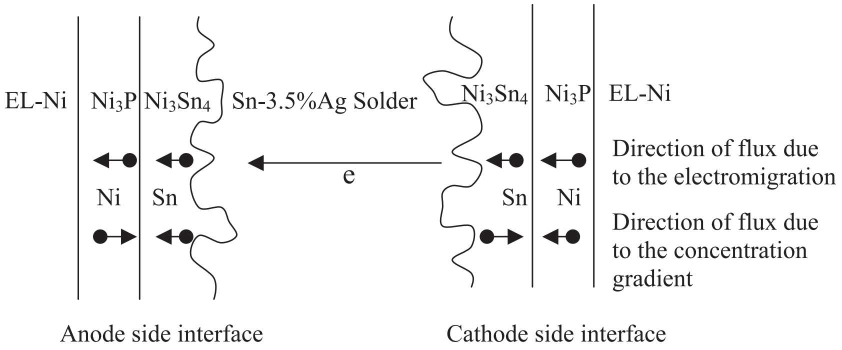

Fig. 8. Schematic illustration for electromigration effect on Ni_3Sn_4 growth in EL-Ni/Sn–3.5% Ag system.

Sn–3.5% Ag system is due to the Ni_3P layer present between the EL-Ni and Ni_3Sn_4. During Ni_3Sn_4 growth, Ni diffuses from EL-Ni to Ni_3P/Ni_3Sn_4 interface through Ni_3P grain boundaries. Thus, at anode side interface, where electrons flow from solder to EL-Ni, current retards the Ni flux through the Ni_3P toward the Ni_3P/Ni_3Sn_4 interface, where as at cathode side interface, where electrons flow from EL-Ni to solder, it retards the Sn flux through the Ni_3Sn_4 towards the Ni_3Sn_4/Ni_3P interface.

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